

# Spin Transition, Cooperative Effects under External Pressure and the High-spin → Low-spin Relaxation

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## Abstract

Iron(II) spin-crossover crystals provide insight into some most interesting phenomena in solid state physics. To fine-tune the zero-point energy difference between the high-spin (HS) and the low-spin (LS) state, external pressure can be used as a tool. The phenomenon of the spin transition, cooperative effects vs. external pressure and the HS → LS relaxation are subjects to be reviewed in this publication with emphasis on the interplay between the internal and the external pressure.

## Keywords

Spin Transition; External and Internal Pressure; High-spin to Low-spin Relaxation; Cooperativity; Single Exponential vs. Sigmoidal Decay; Potential Wells

## Introduction

Iron(II) as a d<sup>6</sup> ion in a particular ligand field undergoes an entropy driven spin transition from the low-spin (LS) to the high-spin (HS) state as the temperature increases. In order to match this condition, the ligands are chosen to provide a positive zero-point energy difference  $\Delta E^0_{\text{HL}} = E_{\text{HS}} - E_{\text{LS}}$ , between the two spin states on the order of magnitude of thermal energies. A significant feature of the LS → HS transition is a large change in the metal-ligand distance, typically 10%. This is not astonishing when the distinct change in the arrangement of the electrons is taken into account, i. e. the promotion of two electrons from non-bonding to antibonding orbitals upon LS → HS transition. The large change in metal-ligand distance is followed by a concomitant large volume change of the complexes. Indeed, the whole crystal expands upon LS → HS transition, or shrinks by undergoing a HS → LS transition, as evidenced by crystallographic measurements (Wiehl *et al.* 1990)

## Results and Discussion

A valuable tool that allows the fine-tuning of the zero-point energy difference between the low-spin and the

high-spin state is the external pressure. A special experimental device has been developed in order to apply hydrostatic Helium pressure to single crystals and to detect the high-spin → low-spin transition by optical absorption spectroscopy as described in reference (Jeftić *et al.*, 1997). Another experimental setup that has been developed in order to study the pressure influence on spin-crossover powdered samples is described in reference (Jeftić *et al.*, 1999). This technique is based on optical reflectivity measurements, Fig. 1 (Hauser *et al.*, 1996) shows the influence of pressure on the zero-point energy difference between the low-spin and the high-spin state. External pressure shifts the two potential wells by the work term  $p\Delta V^0_{\text{HL}}$ .

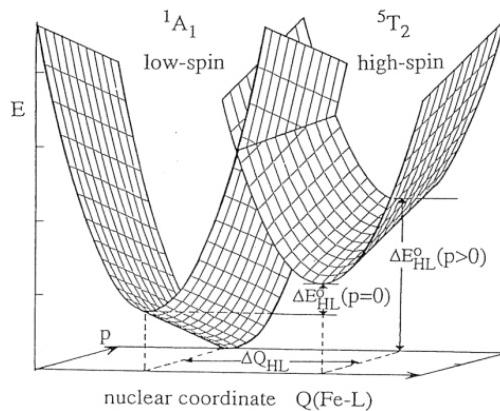


FIGURE 1 SCHEMATIC REPRESENTATION OF THE POTENTIAL WELLS OF THE HIGH-SPIN AND THE LOW-SPIN STATE IN AN IRON (II) SPIN-CROSSOVER COMPOUND AS A FUNCTION OF PRESSURE. P STANDS FOR EXTERNAL PRESSURE, BUT CAN ALSO BE INTERPRETED AS A BUILD-UP OF AN INTERNAL PRESSURE DUE TO ELASTIC INTERACTIONS. (Hauser *et al.* 1996)

Other perturbation techniques to induce the HS → LS transition are based on light of different wavelengts to induce LIESST (Light Induced Exited Spin State Trapping) or reverse-LIESST (Decurtins *et al.*, 1991) or the temperature change. These perturbations may as well be used for fine-tuning the zero point energy difference between the two spin states.

How does the above mentioned shift relate to the cooperative interactions? In neat spin-crossover systems, the interactions between spin-changing molecules are considered to be of elastic origin. The elastic interactions may be pictured as an internal or chemical pressure depending upon the distribution of complexes between HS and LS states (Hauser *et al.*, 1996). Electronically, the complexes are still described individually with the surroundings modulating  $\Delta E^{\text{LS}}$ . In mean-field approximation (Slusher *et al.*, 1972; Speiering *et al.*, 1982; Köhler *et al.*, 1990), this modulation only depends on the average number of complexes in a given state. A large fraction of small LS complexes leads to a contraction of the crystal lattice and thus an increasing internal pressure which further stabilizes the LS state; on the other hand, a large fraction of HS complexes leads to an expansion of the crystal lattice and thus a decreasing internal pressure which, in turn, stabilizes the HS state. Therefore, transition curves in neat materials are generally steeper than those in diluted mixed crystals (Speiering *et al.*, 1982; Martin *et al.*, 1994). For values of the so-called interaction parameter  $\Gamma$  above some critical value, a thermal hysteresis may be observed (Köhler *et al.*, 1990).

The concept of an internal pressure accounts for isotropic, long-range interactions only. Such long-range interactions in the form of an image pressure (Eshelby, 1956) are always present in finite crystals and tend to stabilize the majority species. In addition to long range interactions, short range interactions are important in explaining the formation of a step in the transition curves of some spin-crossover compounds (Willenbacher *et al.*, 1988; Speiering *et al.*, 1999). Short-range interactions can enhance the effect of the long-range interactions, in which case the two contributions to the interaction are very difficult to separate experimentally. On the other hand, they can act in such a way as to favor the formation of HS-LS pairs (Jung *et al.*, 1996), and in that case steps in the thermal transition curves may be observed, even for crystal structures where all complexes have crystallographically equivalent lattice sites (Köppen *et al.*, 1982; Real *et al.*, 1992). Short-range interactions also affect the HS  $\rightarrow$  LS relaxation.

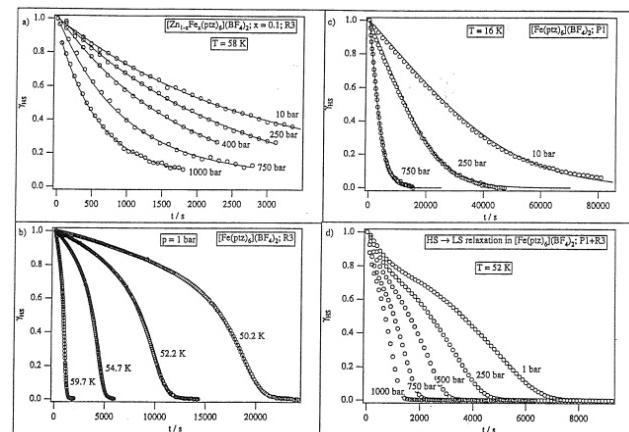
The influence of the external pressure on the HS  $\rightarrow$  LS relaxation has been studied at ambient temperatures by Adler *et al.* for various iron(II) spin-crossover compounds (Adler *et al.*, 1989), and an increase in the rate constant  $k_{\text{HL}}$  by a factor of less than or equal to 2 per kbar has been determined. We studied the HS  $\rightarrow$

LS relaxation in the mixed and the neat  $[\text{Zn}_{1-x}\text{Fe}_x(\text{ptz})_6](\text{BF}_4)_2$ ,  $x = 0.1$  and 1, system over a much larger temperature range, from 15 K to about 200 K. External pressure applied to the mixed system provided insight into the behavior of individual spin-crossover molecules imbedded into an inert zinc host lattice. In diluted system, the relaxation is single exponential and it remains so under external pressure. An exponential increase with pressure is observed according to

$$k_{\text{HL}} \sim \exp(\beta p) \quad (1)$$

where  $p$  stands for external pressure (Jeftić *et al.*, 1997).  $\beta$  is the acceleration factor due to external pressure. At low temperatures in the tunneling region and in the strong coupling limit, it can be expressed as

$$\beta(T \rightarrow 0) \approx \beta_n \ln S - \beta_s. \quad (2)$$



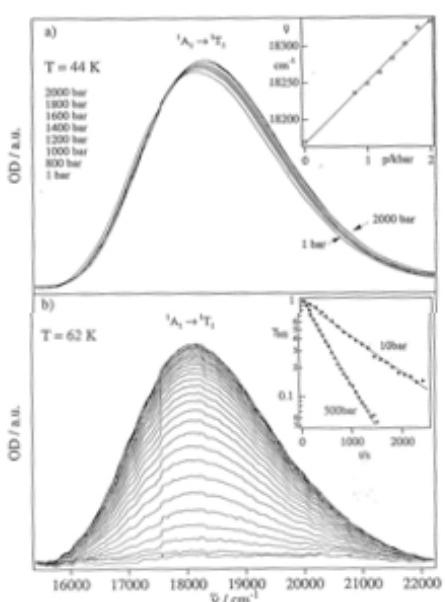
**Figure 2:** HS  $\rightarrow$  LS relaxation curves of a) diluted system  $[\text{Zn}_{1-x}\text{Fe}_x(\text{ptz})_6](\text{BF}_4)_2$ ,  $x = 0.1$ , in rhomboedric phase at 58 K at elevated pressures, b) neat system  $[\text{Fe}(\text{ptz})_6](\text{BF}_4)_2$ , in rhomboedric phase at various temperatures and pressure of 1 bar, c) neat system in triclinic phase at 16 K and elevated pressures, d) neat system with both rhomboedric and triclinic components at 52 K for elevated pressures from 1 bar to 1000 bar (jeftić *et al.* 1997).

The external pressure increases the energy difference between the HS and the LS state for the work term  $p\Delta V^{\text{HL}}$ , and the contribution to  $\beta$  coming from the vertical displacement of the potential wells,  $\beta_n$ , is given by

$$\beta_n \approx \Delta V^{\text{HL}} / \hbar \omega \approx 0.5 \text{ kbar}^{-1} \quad (3)$$

with  $\Delta V^{\text{HL}} = 26 \text{ \AA}^3/\text{complex}$  (Jeftić *et al.* 1996). This corresponds to an increase in  $\Delta E^{\text{HL}}$  of  $130 \text{ cm}^{-1}/\text{kbar}$  which is supported by a spectroscopic observation of the linear shift to the higher energies of the maximum of the  ${}^1\text{A}_1 \rightarrow {}^1\text{T}_1$  low-spin band with increasing pressure. The shift is  $85 \text{ cm}^{-1}/\text{kbar}$  which is slightly smaller but still within the 1 : 1 relationship between  $10Dq^{\text{LS}}$  and  $\Delta E^{\text{HL}}$  proposed by Clack and Smith (Clack *et al.*, 1974). The change in bond length difference between the two spin states has been estimated as  $10^{-3}$

$\text{\AA}/\text{kbar}$ , and it follows  $\beta_s = -0.5 \text{ kbar}^{-1}$  (Jeftić *et al.* 1996). The resulting value for  $\beta(T \rightarrow 0)$  of about  $2.5 \text{ kbar}^{-1}$  is in a good agreement with the experimental value of  $\sim 2.8 \text{ kbar}^{-1}$  (Jeftić *et al.*, 1997). In the cited reference, this relaxation kinetics has been studied in detail for neat and diluted Fe(II) spin-crossover crystals or inbedded into the Zn matrix. One can observe that exponential curves represent the lack of cooperativity in diluted systems while the sigmoidal curves are a signature of cooperative effects as can be seen in Figure 2. The details of the shift of absorption spectra under the influence of pressure is given in Figure 3 (Jeftić *et al.*, 1996) and the corresponding relaxation kinetics is described in detail in this reference.



**Figure 3** a) Single crystal absorption spectra of diluted system  $[\text{Zn}_1-x\text{Fe}_x(\text{ptz})_6](\text{BF}_4)_2$ ,  $x = 0.1$ , in the region of the spin-allowed  $^1\text{A}_1 \rightarrow ^1\text{T}_1$  transition at 44 K and external pressures between 1 bar and 2 kbar. Inset: Band maximum as function of pressure. (□) exponential, (—) linear fit b) HS  $\rightarrow$  LS relaxation at 62 K and 0.5 kbar following the light induced population of the HS state (interval between spectra 30 s). Inset : relaxation curves at 10 bar ( $\blacklozenge$ ) and 0.5 bar ( $\circ$ ) and exponential fits (Jeftić *et al.*, 1996).

The buildup of an internal pressure in the neat system during the HS  $\rightarrow$  LS relaxation is proportional to the LS fraction, and according to the energy gap law, the relaxation rate constant is given by

$$k_{\text{HL}} \sim \exp(-\alpha \gamma_{\text{LS}}). \quad (4)$$

To compare the influence of external pressure on the complexes in the diluted system with the internal pressure that emerges in the concentrated system in the tunneling region, we draw a parallel between  $\beta(T \rightarrow 0)$  and  $\alpha(T \rightarrow 0)$ . The value of  $\beta(T \rightarrow 0)$  of about  $2.8 \text{ kbar}^{-1}$  compared to the self-acceleration factor  $\alpha(T \rightarrow 0)$  of about 5, describing the cooperative effects in  $[\text{Fe}(\text{ptz})_6](\text{BF}_4)_2$  based on the  $\gamma_{\text{LS}}$  dependent relaxation

rate constant of Eq. (1), shows that an external pressure of about 2 kbar would accelerate the HS  $\rightarrow$  LS relaxation in the mixed crystal by the same amount as the elastic interactions accelerate it in the neat material. The neat spin-crossover compound as well as the zinc host of the investigated system crystallizes in the high-symmetry space group  $R\bar{3}$  [18] and the reaction coordinate for the HS  $\rightarrow$  LS relaxation is well described by the totally symmetric metal-ligand stretch vibration. In the close to perfectly octahedral coordination of the complex, a nearly isotropic change in volume takes place and the mean field approximation is valid. In systems where anisotropic contributions are larger, a more sophisticated treatment is needed as proposed in Refs. [Willenbacher *et al.*, 1988; Spiering *et al.* 1989, Jung *et al.* 1996].

The neat compound  $[\text{Fe}(\text{ptz})_6](\text{BF}_4)_2$  (ptz = 1-propyltetrazole) belongs to the class of spin-crossover compounds with a hysteresis, where the thermal spin transition is accompanied by a crystallographic phase transition (Franke *et al.*, 1982). The transition temperatures are  $T_c^\downarrow = 128 \text{ K}$  and  $T_c^\uparrow = 135 \text{ K}$ . At temperatures above  $T_c^\uparrow$ , the Fe(II) complexes are predominantly in the HS state and the compound belongs to space group  $R\bar{3}$ . Below  $T_c^\downarrow$ , the complexes are predominantly in the LS state and the probable space group is now  $P\bar{1}$  (Wiehl, 1993). From a temperature dependent powder diffraction study, a difference in volume between the HS and the LS state of  $50 \text{ \AA}^3 / \text{molecule}$  was determined (Wiehl *et al.*, 1990). This value is corrected for the normal thermal expansion of the lattice, but it includes the effects of both the spin transition and the phase transition. Making use of the phenomenon of light-induced spin-crossover (Decurtins *et al.*, 1985; Hauser, 1995; Gütlich *et al.*, 1994), the difference in volume between the HS state and the LS state at 20 K in the low-symmetry phase was found to be  $35 \text{ \AA}^3/\text{molecule}$  (Wiehl, 1993).

The simultaneous study of the internal and the external pressure influencing the HS  $\rightarrow$  LS relaxation has been undertaken in  $[\text{Fe}(\text{ptz})_6](\text{PF}_6)_2$  (Jeftić *et al.*, 1997). This system crystallizes in the  $P\bar{1}$  space group. In the first approximation, the distortion from the octahedral coordination of the iron complexes is negligible. The structure is ordered in layers orthogonal to the pseudo-3-fold axis of rotation which seems to be a general structural feature within the  $[\text{Fe}(\text{Rtz})_6](X)_2$  series (R = methyl, ethyl, propyl; X =  $\text{BF}_4^-$ ,  $\text{PF}_6^-$ ) (Wiehl, 1993; Hinek *et al.*, 1996). The interaction constant  $\Gamma$  is large resulting in the extremely steep spin transition, but it is still below the critical value

above which hysteresis behavior due to elastic interactions would be observed. The self-acceleration factor  $\alpha$  ( $T \rightarrow 0$ ) in this system is about 2 (Hauser, 1995) and the acceleration factor due to the external pressure  $\beta$  ( $T \rightarrow 0$ ) is about 2 kbar<sup>-1</sup>, thus 1 kbar external pressure accelerates the HS  $\rightarrow$  LS relaxation in the same way as the cooperative effects do (Jeftić *et al.*, 1997).

The two effects add up, resulting in the proportionality:

$$k_{HL} \sim \exp(\alpha \gamma_{LS} + \beta p). \quad (5)$$

Within experimental error,  $\alpha$  and  $\beta$  are independent of each other. The dependence of the interaction constant  $\Gamma$  on the external pressure up to 1 kbar is negligible.

The influence of the external and the internal pressure on the ligand-field strength  $10Dq$  can be spectroscopically evidenced. The shift to higher energies of the maximum of the  $^1A_1 \rightarrow ^1T_1$  low-spin band with increasing external pressure at low temperatures,  $\Delta\nu_p$  differs considerably from the energy shift due to the internal pressure which was determined during the relaxation at a constant temperature and ambient pressure,  $\Delta\nu_\gamma$ . This is explained on the basis of the crystal packing. The layer structure results in a relatively strong anisotropy of the compressibility. Both external and internal pressures primarily change the bond lengths. At the same time, the external pressure can compress the complexes along the pseudo trigonal axes resulting in a distortion of the pseudo-octahedron in this direction. On the other hand, the internal pressure would rather expand the pseudo-octahedron along the trigonal axis. During the spin transition from the smaller LS state to the bigger HS state, the complexes have less space to expand in the plane perpendicular to the axis with "harder" contacts between them. Therefore, the influence of internal and external pressure on vibrations other than the totally symmetric Fe-N stretching vibrations varies distinctly, followed by different shifts and splitting, and making the quantitative comparison of  $\Delta\nu_p$  and  $\Delta\nu_\gamma$  difficult.

## Conclusion

In conclusion, it can be said that the effects of external pressure and cooperative effects on the HS  $\rightarrow$  LS relaxation in  $[Zn_{1-x}Fe_x(ptz)_6](BF_4)_2$ ,  $x=0.1$  and  $[Fe(ptz)_6](BF_4)_2$  can be explained consistently, showing that there is a physical reality behind the concept of an internal pressure. This is due to the fact that the zinc host as well as the neat spin-crossover compound

crystallizes in the high-symmetry space group R̄3 (Franke *et al.*, 1982). Thus, the reaction coordinate for the HS  $\rightarrow$  LS relaxation is very well described by the totally symmetric metal-ligand stretch vibration, which in the almost perfectly octahedral coordination of the complex corresponds to an almost isotropic change in volume. In systems of lower symmetry where the elastic interaction has large anisotropic contributions (Spiering *et al.*, 1989; Willenbacher *et al.* 1988) the above consistency is not to be expected.

The external pressure is a valuable tool in understanding the spin transition in molecular solids. It would be interesting to investigate the dependence of the internal pressure on the structural anisotropy in spin-crossover materials and thus correlating the crystallographic structure with the influence of external pressure for a series of materials. It is interesting to note that different structural studies are undertaken in order to understand the interplay between the spin transition and crystallographic phase transition, as well as the studies under influence of light which is the most interesting external perturbation in understanding various photophysical processes in spin transition solids (Goujon *et al.*, 2006; Desaix *et al.*, 1998; Varret *et al.* 2007).

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